"Mechanisms of Inorganic Reactions, a study of metal complexes in solution". 1967

The results of numerous investigations for the first transition series show that, regardless of the nature of the donor group, the so-called *natural order*[97] of the stability of complexes of bivalent transition metals is $Mn < Fe < Co < Ni < Cu > Zn$. Only in a very few cases have deviations from this order been observed. It has been found, for example, that the stability of $Fe(phen)_3^{3+}$ is greater than expected and, furthermore, that the value of K_3 for the addition of the third group is larger than that of either K_1 or K_2.[98] This is attributed to an electronic rearrangement, for it was shown[99] that the bis complex, $Fe(phen)_2X_2$, is paramagnetic, whereas the tris complex, $Fe(phen)_3^{2+}$, is diamagnetic.

If we attempt to list the other metal ions in the order of increasing stability of their complexes, this turns out to be impossible unless the ligand is specified. In the same way, it is not possible to put the common ligands into an order of complexing ability unless a reference metal ion is specified.

Hard and Soft Acids and Bases[100]

Various metal ions fall into two categories: (1) those binding strongly to bases which bind strongly to the proton, that is, basic in the usual sense; (2) those binding strongly to highly polarizable or unsaturated bases, which often have negligible proton basicity. Division into the two categories is not absolute and intermediate cases occur, but the classification is reasonably sharp and appears to be quite useful. It is convenient to divide bases also into two categories, those that are polarizable or "soft," and those that are non-polarizable or "hard." It is possible for a base to be both soft and strongly binding toward the proton, e.g., sulfide ion. Still it is generally true that hardness is associated with good proton binding. For example, for the bases in which the coordinating atom is from Groups V, VI, and VII (the great majority of all bases), the atoms fluorine, oxygen, and nitrogen are the hardest in each group and also the most basic to the proton.
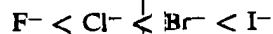
It has long been recognized[101] that metal ions can be divided into two classes depending on whether they form their most stable complexes with the first ligand atom of each group, class (a), or whether they form their most stable complexes with the second or a subsequent member of each group, class (b). Thus, for class (a) metal ions the order of stability is as follows:

$$F^- > Cl^- > Br^- > I^-$$

$$O \gg S > Se > Te$$

$$N \gg P > As > Sb > Bi$$
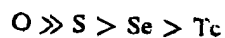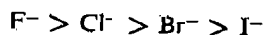
24   Introduction

Whereas for class (b) the order of stability is

$$F^- < Cl^- < Br^- < I^-$$
$$O \ll S \sim Se \sim Te$$
$$N \ll P > As > Sb > Bi$$

Class (a) metal ions bind best to the least polarizable (hardest) atom of a family, whereas class (b) metal ions bind best to a more polarizable (softer) atom of the same family. Notice that it is not always the most polarizable (softest) atom which forms the most stable complexes with a class (b) metal ion. The reason for this is that many bases, such as the stibines, are weak bases toward all metal ions. Their complexes with class (b) metals will usually be much more stable than their complexes with class (a) acids, however.

Other Lewis acids can be examined to see whether the stability of their acid-base adducts corresponds to class (a) or class (b) behavior. The acid-base or donor-acceptor[102] adducts which they form may be inorganic or organic molecules, complex ions, or charge-transfer complexes.

Table 1.6 contains a list of all generalized acids for which sufficient information can be found in the literature to enable a choice between class (a) and class (b) to be made. In classifying Lewis acids, the criterion previously used[101] was followed whenever possible, that is, to compare the stabilities of fluorine versus iodine, oxygen versus sulfur, and nitrogen versus phosphorus type complexes. When such comparisons are not feasible, other criteria may be used.[100] One is that class (b) acids will complex readily with a variety of soft bases that are of negligible proton basicity. These include CO, olefins, aromatic hydrocarbons, and the like.

The common characteristics of the two classes of Lewis acids are easily discernible from Table 1.6. The features which bring out class (a) behavior are small size, high positive oxidation state, and no easily distorted outer electrons. Class (b) behavior is associated with a low or zero oxidation state, with large size, and with easily distorted outer electrons. Both metals and non-metals can be either (a) or (b) type acids, depending or their charge and size. Since the features which promote class (a) behavior are those leading to low polarizability, and those which create type (b) behavior lead to high polarizability, it is convenient to call class (a) acids "hard" and class (b) acids "soft." We then have the useful generalization that *hard acids prefer to associate with hard bases, and soft acids prefer soft bases.*¶

¶ It is not implied that complexes of hard acids and soft bases, or vice versa, cannot exist and be quite stable. For example, CH_3 is a soft base yet compounds such as $Mg(CH_3)_2$ can easily be made. Nevertheless this compound is thermodynamically unstable to hydrolysis, whereas $Hg(CH_3)_2$ is thermodynamically stable to hydrolysis.

Polarizability is simply a convenient property to use as a classification. It may well be that other properties which are roughly proportional to polarizability are more responsible for the typical behavior of the two classes of acids. For example, a low ionization potential is usually linked to a high polarizability, and a high ionization potential to a low polarizability. Hence, ionization potential or the related electronegativity might be the important property. Unsaturation, with the possibility of accept or

Table 1.6   Classification of Lewis acids

Hard	Soft
H^+, Li^+, Na^+, K^+	Cu^+, Ag^+, Au^+, Tl^+, Hg^+
Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Mn^{3+}	Pd^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}, CH_3Hg^+,
	$Co(CN)_5^{2-}$, Pt^{4+}, Te^{4+}
Al^{3+}, Sc^{3+}, Ga^{3+}, In^{3+}, La^{3+}	Tl^{3+}, $Tl(CH_3)_3$, BH_3, $Ga(CH_3)_3$, $GaCl_3$,
N^{3+}, Gd^{3+}, Lu^{3+}	GaI_3, $InCl_3$
Cr^{3+}, Co^{3+}, Fe^{3+}, As^{3+}, Ce^{3+}	RS^+, RSe^+, RTe^+
Si^{4+}, Ti^{4+}, Zr^{4+}, Th^{4+}, Pu^{4+}	I^+, Br^+, HO^+, RO^+
UO_2^{2+}, $(CH_3)_3Sn^{2+}$, VO^{2+}, MoO^{3+}	I_2, Br_2, ICN, etc.
$BeMe_2$, BF_3, $B(OR)_3$	trinitrobenzene, etc.
$Al(CH_3)_3$, $AlCl_3$, AlH_3	chloranil, quinones, etc.
RPO_2^+, $ROPO_2^+$	tetracyanoethylene, etc.
RSO_2^+, $ROSO_2^+$, SO_3	O, Cl, Br, I, N
I^{7+}, I^{5+}, Cl^{7+}, Cr^{6+}	M^0 (metal atoms)
RCO^+, CO_2, NC^+	bulk metals
HX (hydrogen-bonding molecules)	CH_2, carbenes

Borderline
Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Sn^{2+}, Sb^{3+}, Bi^{3+}, Rh^{3+}, Ir^{3+}, $B(CH_3)_3$, SO_2,
NO^+, Ru^{2+}, Os^{3+}, R_3C^+, $C_6H_5^+$, $Ga H_3$

bonding in the acid-base complex, and ease of reduction, favoring strong electron transfer to the acid, are also associated with high polarizability.

   While considerable variation can exist because of the effect of overall charge, the usual stability order overall for class (b) metal ions is $S \sim C > I > Br > Cl > N > O > F$. For class (a) metal ions a strong inversion of this order occurs, so that often only oxygen and fluorine complexes can be obtained in aqueous solution.[103] It may be noted that the order given above is that of increasing electronegativity.**

   ** Table 3.4 lists a series of stability constants for various ligands for the typical soft acid CH_3Hg^+.